A Simple and Effective Co-Catalyst for Ring-Closing Enyne Metathesis Using Grubbs I type Catalysts: A Practical Alternative to “Mori’s Conditions”

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CONTENTS

General experimental details .................................................. S2
Preparation of 1-[2H$_2$]-deuterated dec-1-ene .......................... S3
Characterisation of RCM-CM products 7a ............................... S5
Preparation of ruthenium alkylidene complexes ....................... S7
RCM of 1a using [2H$_2$]-decene co-catalyst (Scheme 4 in comm) S9
Kinetics of alkene exchange between ruthenium alkylidenes .......... S13
Kinetics of RCM of enyne 1a using alkene co-catalysts .......... S15
Kinetics of RCM of enyne 1a using allyl bromide as co-catalyst S18
References ............................................................................. S18
General experimental details

**Solvents:** Solvents were obtained from an *Anhydrous Engineering* alumina column-based solvent drying system. Tetrahydrofuran was dried further by distillation in bulk from sodium and benzophenone under an inert (N$_2$) atmosphere. Methanol was dried over charged 3Å molecular sieves and degassed by freeze-thaw cycling. Dry dichloromethane was degassed by freeze-thaw cycling. Dry dimethylformamide was purchased from Fluka and used without further purification. [2H$_2$]-Dichloromethane and [2H$_6$]-benzene for NMR studies was purchased from *Cambridge Isotope Laboratories* and distilled in small quantities from molecular sieves (3Å) under an inert (N$_2$) atmosphere immediately prior to use.

**Materials:** All starting materials and reagents were obtained from commercial sources (Aldrich, Lancaster, Alfa Aesar, Fluka, Acros, Strem, TCI Chemicals and Avacado) unless otherwise stated.

**Techniques:** All air-sensitive manipulations were conducted under an inert (N$_2$) atmosphere using standard Schlenk-line techniques. Catalytic runs were performed in a *Radleys Carousel* reactor under an inert (N$_2$) atmosphere. Samples for GC or GC-MS analysis were obtained by removal of a small quantity ($\approx$ 20 µL) of the reaction mixture by gas-tight syringe, followed by quenching with triphenylphosphine. Each sample was then filtered through a silica plug into a GC vial. Selected samples were re-run to make sure that the reactions had stopped turning over after quenching.

**Analysis:** Gas Chromatography: GC samples were analysed on Hewlett Packard HP5890 (GC) with flame ionisation detector (detector gases – hydrogen at 30 cm$^3$ min$^{-1}$, air at 400 cm$^3$ min$^{-1}$, helium at 20 cm$^3$ min$^{-1}$; split ratio 1:50; carrier gas – helium at 1 cm$^3$ min$^{-1}$; column – Alltech EC™, 30 m x 0.25 mm ID, 0.25 µm film thickness) and Varian Saturn 2200 (GC/MS).

Column Chromatography: BDH silica gel 60-120 mesh. Thin Layer Chromatography: 0.25mm, Merck silica gel 60 F254 developed with 2% KMnO$_4$.

**NMR:** NMR spectra were obtained on Varian 400, Lambda 300, JEOL ECP300 and ECP400 instruments utilising the $^2$H-signal from the solvent as the frequency lock. $^1$H and $^{13}$C($^1$H) NMR spectra were referenced internally to the solvent, or to TMS (0 ppm) for samples dissolved in CDC$_3$. The following abbreviations are used for NMR signal assignments: s (singlet), d (doublet), t (triplet), q (quartet), qu (quintet), sx (sextet), sep (septet), m (multiplet), br (broad).

InfraRed (solid or neat liquid phase): Perkin Elmer Spectrum One. The position of bands are quoted as wavenumbers (cm$^{-1}$) and described using the following abbreviations: weak (w), strong (s) and broad (br).

**Mass Spectrometry:** High-resolution mass spectra (HRMS) [Positive Ion EI and CI or Electrospray (ES)] were obtained at the Mass Spectrometry Laboratory in the University of Bristol School of Chemistry.

**Accurate weights:** Obtained with a Sartorius BP 211 balance.
1-[\textsuperscript{2}H\textsubscript{1}]\text{-1-decyne}

n-BuLi (16.0 cm\textsuperscript{3}, 39.8 mmol, 2.5M in hexane) was added dropwise to a solution of decyne (5.0 cm\textsuperscript{3}, 36.2 mmol) in THF (50 cm\textsuperscript{3}) at -78 °C. The solution was stirred for 20 minutes and deuterium oxide (1.0 cm\textsuperscript{3}, 52.0 mmol) was added via syringe. The solution was allowed to reach room temperature and the mixture was extracted with diethyl ether (3 × 30 cm\textsuperscript{3}). The combined organic layers were washed with aqueous 0.1M HCl (30 cm\textsuperscript{3}) and brine (30 cm\textsuperscript{3}), dried over anhydrous MgSO\textsubscript{4}, filtered and concentrated under reduced pressure to afford 1-[\textsuperscript{2}H\textsubscript{1}]\text{-1-decyne as a colourless oil (4.6 g, 91 %); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 23 °C, TMS) δ = 2.18 (t, \textsuperscript{3}J(H,H) = 6.8 Hz, 2H, C(3)-H), 1.92 (t, 0.03H, residual C(1)-H), 1.51 (qu, 2H, \textsuperscript{3}J(H,H) = 6.8 Hz, C(4)-H), 1.40-1.28 (br m, 10H, C(5-9)-H), 0.88 (t, \textsuperscript{3}J(H,H) = 6.2 Hz, 3H, C(10)-H); \textsuperscript{[\textsuperscript{2}H\textsubscript{1}]\text{-incorporation: > 97% (alkyne); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 23 °C) δ = 84.3 (t, \textsuperscript{2}J(C,D) = 7.3 Hz, C(2)), 67.8 (t, \textsuperscript{1}J(C,D) = 37.4 Hz, C(1)), 31.7, 29.3, 28.7, 28.5, 22.6 (C(4-9)), 18.5 (C(3)), 14.1 (C(10)). Data is consistent that previously published.\textsuperscript{S1}

1-[\textsuperscript{2}H\textsubscript{2}]\text{-dec-1ene}

1-[\textsuperscript{3}H\textsubscript{1}]\text{-Dec-1-yne (4.0 g, 28.8 mmol) was added to a suspension of Schwarz reagent (9.65 g, 37.4 mmol) in DCM (20 cm\textsuperscript{3}) at -10 °C. The mixture was stirred for 20 minutes to give a bright yellow transparent solution. Deuterium oxide (5.0 cm\textsuperscript{3}) was then added and the mixture was stirred vigorously for a further 10 minutes at room temperature. The organic layer was separated and passed through a short plug (ca. 5cm) of silica-gel. The solution was concentrated under reduced pressure to afford a pale yellow oil. Isolation by Kogelröh distillation (180 °C, 760 torr) afforded 1-[\textsuperscript{3}H\textsubscript{2}]\text{-dec-1ene as a colourless oil (3.3 g, 82%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 23 °C, TMS) δ = 5.80 (m, 1H, C(2)-H), 4.92-4.88 (m, 0.02H, residual C(1)-H), 2.07 (dt, 2H, \textsuperscript{3}J(H-H) = 7.5, \textsuperscript{3}J(H-H) = 6.7 Hz, C(3)-H), 1.31 (br m, 12H, C(4,5,6,7,8,9)-H), 0.92 (t, \textsuperscript{3}J(H,H) = 7.2 Hz, 3H, C(10)-H); \textsuperscript{[\textsuperscript{3}H\textsubscript{2}]\text{-incorporation: > 98%; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 23 °C) δ = 139.0 (C(2)), 113.8 (quint, \textsuperscript{1}J(C,D) = 23.4 Hz, C(1)), 33.7 (C(3)), 32.2 (C(8)), 29.5, 29.3, 29.2, 29.1 (C(4-7)), 22.8 (C(9)), 14.0 (C(10)). Data is consistent that previously published.\textsuperscript{S2}

1,2-dibromodecane
Bromine was added dropwise to a stirred solution of dec-1-ene (100 mg, 0.72 mmol) in DCM (10 cm³) until a dark red colour persisted. The solution was then concentrated under vacuum to afford 1,2-dibromodecane as a pale yellow oil (210 mg, 97%); \(^1\)H NMR (300 MHz, CDCl₃, 23 °C, TMS): δ = 4.17 (m, 1H, C(2)-H), 3.84 (dd, ^3^J(H,H) = 5.0, ^3^J(H,H) = 10.3 Hz, 1H, C(1)-H), 3.62 (t, ^3^J(H,H) = 10.3 Hz, 1H, C(1)-H), 1.81-1.71 (m, 2H, C(3)-H), 1.37-1.19 (br m, 12H, C(4-9)-H), 0.88 (t, ^3^J(H,H) = 6.4 Hz, 3H, C(10)-H); \(^13^\)C NMR (75 MHz, CDCl₃, 23 °C) δ = 53.3 (C(2)), 36.4 (C(1)), 36.1 (C(3)), 31.9 (C(8)), 29.5, 29.3, 28.9, 26.8 (C(4-7)), 22.8 (C(9)), 14.2 (C(10)); IR (neat): v = 2927 (w), 2850, 1738 (w), 1366 (s), 1228 (w) cm⁻¹; MS (EI) m/z (%): 299 [MH]+ (9), 221 (67), 179 (24), 165 (19), 137 (20). Data is consistent with previously published.\(^{S3}\)

1,1-[\(^2\)H]-1,2-dibromodecane

Bromine was added dropwise to a stirred solution of [\(^2\)H]_2-1-decene (100 mg, 0.71 mmol) in DCM (10 cm³) until a dark red colour persisted. The solution was then concentrated under vacuum to afford 1,1-[\(^2\)H]-1,2-dibromodecane as a pale yellow oil (208 mg, 96%); \(^1\)H NMR (300 MHz, CDCl₃, 23 °C, TMS): δ = 4.16 (br d, ^3^J(H,H) = 8.9 Hz, 1H, C(2)-H), 3.84 (m, 0.03H, residual C(1)-H), 3.62 (m, 0.03H, C(1)-H), 1.83-1.71 (m, 2H, C(3)-H), 1.38-1.19 (br m, 12H, C(4-9)-H), 0.88 (t, ^3^J(H,H) = 6.6 Hz, 3H, C(10)-H); \(^1\)H incorporation: > 97%; \(^13^\)C NMR (75 MHz, CDCl₃, 23 °C) δ = 53.3 (C(2)), 36.3 (qu, ^1^J(C,D) = 22.5 Hz, C(1)), 36.0 (C(3)), 31.9 (C(8)), 29.5, 29.4, 28.9, 26.7 (C(4-7)), 22.8 (C(9)), 14.2 (C(10)); IR (neat): v = 2929 (w), 2850, 1738 (w), 1366 (s), 1228 (w) cm⁻¹; MS (EI) m/z (%): 301 [MH]+ (8), 223 (36), 181 (45), 167 (73), 139 (57).

[\(^2\)H]-1,1-dimethylcarboxylate-3-vinyl-cyclopent-3-ene [\(^2\)H]-2a

The compound was prepared in situ by RCM of the corresponding enyne [\(^2\)H]-1a
\(^1\)H NMR (400 MHz, CDCl₃, 23 °C, TMS) δ = 6.45 (m, 0.03H, C(6)-H), 5.56 (d, ^3^J(H,H) = 1.8 Hz, 1H, C(4)-H), 5.09 (d, ^2^J(H,H) = 2.5 Hz, 2H, C(7)-H), 3.73 (s, 0.01H, residual C(4)-(CO₂Me)₂), 3.18 (d, ^3^J(H,H) = 1.8 Hz, 2H, C(5)-H), 3.14 (s, 2H, C(2)-H); \(^1\)H incorporation: > 97% (C(6)-H), > 99% (malonate methyl groups); \(^13^\)C NMR (100 MHz, CDCl₃, 23 °C) δ = 172.5 (C(2 × C=O)), 139.9 (C(3)), 132.0 (t, ^1^J(C,D) = 23.4 Hz, C(6)), 126.8 (C(4)), 115.0 (C(7)), 58.6 (C(1)), 52.2 (septet, ^1^J(C,D) = 22.6 Hz, C(2 × CD₃)), 40.9 (C(5)), 39.2 (C(2)).
Ring-Closing Metathesis - Cross-Metathesis Products 7a

Dimethyl 3-((E)-pent-1-enyl)cyclopent-3-ene-1,1-dicarboxylate, 279

\[
\begin{align*}
1^\text{H} \text{ NMR} & (300 \text{ MHz, CDCl}_3, 23 ^{\circ}\text{C, TMS}) \delta = 6.14 (d, ^3J(H,H)_{trans} = 15.6 \text{ Hz, 1H, C(1')-H}), 5.56 (dt, ^3J(H,H)_{trans} = 15.6, ^3J(H,H) = 6.9 \text{ Hz, 1H, C(2')-H}), 5.40 (s, 1H, C(4)-H), 3.72 (s, 6H, C(1)-(CO_2Me)_2-H), 3.12 (br s, 2H, C(5)-H), 2.05 (dt, ^3J(H,H) = 6.9, ^3J(H,H) = 7.1 \text{ Hz, 2H, C(3')-H}), 1.39-1.36 (m, 2H, C(4')-H), 0.87 (t, ^3J(H,H) = 6.9 \text{ Hz, 3H, C(5')-H}); ^13\text{C} \text{ NMR} (75 \text{ MHz, CDCl}_3, 23 ^{\circ}\text{C}) \delta = 172.7 (C(2 \times \text{C=O})), 139.7 (C(3)), 132.6 (C(2')), 125.9 (C(4)), 123.9 (C(1')), 60.2 (C(1)), 58.8 (C(5)), 52.9 (C(2 \times \text{CH}_3)), 40.8 (C(2)), 39.9 (C(3')), 22.5 (C(4')), 13.8 (C(5')); \text{IR (neat): } v = 2930 (w), 1732 (s, C=O), 1251 (s) \text{ cm}^{-1}; \text{MS (EI) m/z: } 253 \text{ [MH]}^+ (45), 193 (100), 149 (17); \text{HRMS (EI) calculated for C}_{14}H_{21}O_4 \text{ [MH]}^+ 253.1440, \text{ found } 253.1447.
\end{align*}
\]

Dimethyl 3-((E)hex-1-enyl)cyclopent-3-ene-1,1-dicarboxylate$^{54}$

\[
\begin{align*}
1^\text{H} \text{ NMR} & (300 \text{ MHz, CDCl}_3, 23 ^{\circ}\text{C, TMS}) \delta = 6.15 (d, ^3J(H,H)_{trans} = 15.8 \text{ Hz, 1H, C(1')-H}), 5.56 (dt, ^3J(H,H)_{trans} = 15.8, ^3J(H,H) = 6.8 \text{ Hz, 1H, C(2')-H}), 5.43 (s, 1H, C(4)-H), 3.75 (s, 6H, C(1)-(CO_2Me)_2-H), 3.13 (br s, 2H, C(5)-H), 2.09 (dt, ^3J(H,H) = 6.8, ^3J(H,H) = 6.9 \text{ Hz, 2H, C(3')-H}), 1.31-1.24 (m, 4H, C(4',5')-H), 0.87 (t, ^3J(H,H) = 6.9 \text{ Hz, 3H, C(6')-H}); ^13\text{C} \text{ NMR} (75 \text{ MHz, CDCl}_3, 23 ^{\circ}\text{C}) \delta = 172.8 (C(2 \times \text{C=O})), 140.1 (C(3)), 133.1 (C(2')), 126.1 (C(4)), 123.9 (C(1')), 60.4 (C(1)), 58.7 (C(5)), 52.9 (C(2 \times \text{CH}_3)), 41.0 (C(2)), 39.8 (C(3')), 32.0 (C(4')), 21.2 (C(5')), 14.1 (C(6')); \text{IR (neat): } v = 2956 (w), 1733 (s, C=O), 1250 (s) \text{ cm}^{-1}; \text{MS (EI) m/z: } 266 \text{ [MH]}^+ (28), 206 (100), 150 (44); \text{HRMS (EI) calculated for C}_{15}H_{22}O_4 \text{ [MH]}^+ 267.1596, \text{ found } 267.1595.
\end{align*}
\]

Dimethyl 3-((E)-oct-1-enyl)cyclopent-3-ene-1,1-dicarboxylate

Page S5
1H NMR (300 MHz, CDCl3, 23 °C, TMS) δ = 6.18 (d, 3J(H,H)trans = 15.6 Hz, 1H, C(1')-H), 5.58 (dt, 3J(H,H)trans = 15.6, 3J(H,H) = 6.8 Hz, 1H, C(2')-H), 5.40 (s, 1H, C(4)-H), 3.74 (s, 6H, C(1)-(CO2Me)2-H), 3.14 (br s, 2H, C(5)-H), 3.10 (br s, 2H, C(2)-H), 2.08 (dt, 3J(H,H) = 6.8, 3J(H,H) = 7.1 Hz, 2H, C(3')-H), 1.38-1.26 (m, 8H, C(4',5',6',7',8',9')-H), 0.90 (t, 3J(H,H) = 6.9 Hz, 3H, C(6')-H); 13C NMR (75 MHz, CDCl3, 23 °C) δ = 172.6 (C(2 × C=O)), 139.2 (C(3)), 132.4 (C(2')), 125.8 (C(4)), 123.8 (C(1')), 60.1 (C(1)), 58.3 (C(5)), 52.9 (C(2 × CH3)), 40.9 (C(2)), 39.3 (C(3')), 33.9, 30.5, 29.6 (C(4',5',6',7',8')), 22.7 (C(7')); IR (neat): v = 2930 (w), 1732 (s, C=O), 1267 (s) cm−1; MS (EI) m/z (%): 295 [MH]+ (54), 235 (45), 149 (33); HRMS (EI) calculated for C17H22O4 [MH]+ 295.1909, found 295.1904.

Dimethyl 3-((E)-dec-1-ethyl)cyclopent-3-ene-1,1-dicarboxylate

1H NMR (300 MHz, CDCl3, 23 °C, TMS) δ = 6.17 (d, 3J(H,H)trans = 15.6 Hz, 1H, C(1')-H), 5.56 (dt, 3J(H,H)trans = 15.6, 3J(H,H) = 6.8 Hz, 1H, C(2')-H), 5.43 (s, 1H, C(4)-H), 3.75 (s, 6H, C(1)-(CO2Me)2-H), 3.12 (br s, 2H, C(5)-H), 3.09 (br s, 2H, C(2)-H), 2.09 (dt, 3J(H,H) = 6.8, 3J(H,H) = 7.1 Hz, 2H, C(3')-H), 1.32-1.25 (m, 12H, C(4',5',6',7',8',9')-H), 0.89 (t, 3J(H,H) = 7.3 Hz, 3H, C(10')-H); 13C NMR (75 MHz, CDCl3, 23 °C) δ = 172.7 (C(2 × C=O)), 139.8 (C(3)), 132.9 (C(2')), 125.7 (C(4)), 123.8 (C(1')), 60.5 (C(1)), 58.8 (C(5)), 53.0 (C(2 × CH3)), 40.9 (C(2)), 40.0 (C(3')), 32.9, 32.0, 29.6, 29.4 (C(4',5',6',7',8')), 22.7 (C(9')), 14.2 (C(10')); IR (neat): v = 2929 (w), 1732 (s, C=O), 1250 (s) cm−1; MS (CI) m/z (%): 323 [MH]+ (51), 291 (14), 262 (100); HRMS (CI) calculated for C18H30O4 [MH]+ 323.2222, found 323.2225.

Dimethyl 3-((E)-tetradec-1-ethyl)cyclopent-3-ene-1,1-dicarboxylate

1H NMR (300 MHz, CDCl3, 23 °C, TMS) δ = 6.15 (d, 3J(H,H)trans = 15.6 Hz, 1H, C(1')-H), 5.59 (dt, 3J(H,H)trans = 15.6, 3J(H,H) = 6.8 Hz, 1H, C(2')-H), 5.40 (s, 1H, C(4)-H), 3.71 (s, 6H, C(1)-(CO2Me)2-H), 3.08 (br s, 2H, C(5)-H), 3.04 (br s, 2H, C(2)-H), 2.01 (dt, 3J(H,H) = 6.8, 3J(H,H) = 7.1 Hz, 2H, C(3')-H), 1.40-1.20 (m, 20H, C(13')-H), 0.88 (t, 3J(H,H) = 6.9 Hz, 3H, C(14')-H); 13C NMR (75 MHz, CDCl3, 23 °C) δ = 172.5 (C(2 × C=O)), 139.7 (C(3)), 132.9 (C(2')), 125.7 (C(4)), 123.8 (C(1')), 60.4 (C(1)), 58.6 (C(5)), 52.7 (C(2 × CH3)), 40.8 (C(2)), 39.8 (C(3')), 32.9, 31.0, 29.8, 29.6, 29.4, 29.3, 27.9 (C(4'-12')), 22.8 (C(13')), 14.0 (C(14')); IR (neat): v = 2931 (w), 1732 (s, C=O), 1267 (s) cm−1; MS (EI) m/z (%): 379 [MH]+ (100), 319 (47), 111 (64), 97 (86); HRMS (EI) calculated for C23H38O4 [MH]+ 379.2848, found 379.2842.
Preparation of ruthenium alkylidene complexes 3b, 3c and 3d

**RuCl₂(=CHCH₂Cl)(PCy₃)₂, 3b**

Allyl chloride (462 mg, 6.1 mmol) was added to a stirred solution of Grubbs Generation I, (benzylidene complex, 3a) (500 mg, 0.61 mmol) in DCM (10 cm³) at -40 °C. The reaction was stirred under an atmosphere of nitrogen for 20 minutes. The solvent was then removed under vacuum to afford a mixture of desired product, 3b and starting material, 3a as a burgundy powder (335 mg, 70%, 85:15 – Product, 3b: Starting Material, 3a); This was the most favourable ratio attainable with further cycles resulting in increased decomposition; **¹H NMR** (300 MHz, CD₂Cl₂, 23 °C) δ = 18.75 (t, ³J(H,H) = 4.8 Hz, 1H, C(1)-H), 4.43 (d, ³J(H,H) = 4.8 Hz, C(2)-H), 2.62-2.44, 1.91-1.63, 1.59-1.38 and 1.34-1.13 (all m, P(C₆H₁₁)₃-H); **³¹P NMR** (300 MHz, CD₂Cl₂, 23 °C) δ = 37.59 (s, PCy₃). Data is consistent that previously published.⁵⁵

**RuCl₂(=CHnBu)(PCy₃)₂, 3c**

A solution of Grubbs Generation I, (benzylidene complex) (500 mg, 0.61 mmol) in DCM (10 cm³) was added to a solution of 1-hexene (510 mg, 6.1 mmol) in DCM (5 cm³) and stirred under an atmosphere of nitrogen for 20 minutes at room temperature. The solvent was then removed under vacuum. This procedure was repeated until all starting material was consumed (as indicated by **³¹P NMR**). The resultant residue was washed with cold methanol (3 × 5 cm³) and dried under vacuum for several hours. 3c was obtained as a deep purple solid (462 mg, 94%); **¹H NMR** (300 MHz, CD₂Cl₂, 23 °C) δ = 19.23 (t, ³J(H,H) = 5.1 Hz, 1H, C(1)-H), 2.73 (dt, ³J(H,H) = 5.1, ³J(H,H) = 5.2 Hz, C(2)-H), 2.60-2.42, 1.93-1.38, 1.35-1.14 and 0.97-0.85 (all m, C(3,4,5)-H and P(C₆H₁₁)₃-H); **³¹P NMR** (300 MHz, CD₂Cl₂, 23 °C) δ = 37.59 (s, PCy₃); **MS (ESI)** m/z: 767 [M-Cl]⁺; **HRMS (ESI)** calculated for C₄₁H₇₆ClP₂Ru [M-Cl]⁺ 767.4148, found 767.4150. 0. Data is consistent that previously published.⁵⁵
A solution of Grubbs Generation I (benzylidene complex) (500 mg, 0.61 mmol) in DCM (10 cm$^3$) was added to a solution of allyl malonate (1.1 g, 6.1 mmol) in DCM (5 cm$^3$) and stirred under an atmosphere of nitrogen for 20 minutes at room temperature. The solvent was then removed under vacuum. This procedure was repeated until all starting material was consumed (as indicated by $^{31}$P NMR). The resultant residue was washed with cold methanol (3 $\times$ 5 cm$^3$) and dried under vacuum for several hours. 3d was obtained as deep purple solid (462 mg, 94%); $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 23 °C) $\delta$ = 18.98 (t, $^3$J(H,H) = 5.1 Hz, 1H, C(1)-H), 3.74 (s, 6H, C(3)-(CO$_2$Me)$_2$-H), 3.26 (t, $^3$J(H,H) = 7.0 Hz, 1H, C(3)-H), 2.52 (m, 2H, C(2)-H), 2.59-2.44, 1.93-1.44 and 1.33-1.14 (all m, P(C$_6$H$_{11}$)$_3$-H); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, 23 °C) $\delta$ = 306.8 (C(1)), 168.9 (2 $\times$ C=O), 56.3 (C(2)), 51.3 (C(2 $\times$ CH$_3$)), 49.3 (C(3)), 31.8 (pseudo t, $^2$J(C,P) = 10.0 Hz, C(1')), 29.4 (C(3',5')), 27.8 (pseudo t, $^3$J(C,P) = 4.5 Hz, C(2',6')), 26.9 (C(4')); $^{31}$P NMR (300 MHz, CD$_2$Cl$_2$, 23 °C) $\delta$ = 36.90 (s, PCy$_3$); IR (neat): $\nu$ = 2929 (w), 2850, 1732 (s, C=O), 1440 (s), 1266 (w) cm$^{-1}$; MS (ESI) m/z: 855 [M-Cl]$^+$; HRMS (ESI) calculated for C$_{43}$H$_{76}$ClO$_4$P$_2$Ru [M-Cl]$^+$ 855.3945, found 855.3961; Anal. Calcd for C$_{43}$H$_{76}$ClO$_4$P$_2$Ru: C, 57.97; H, 8.60. Found: C, 58.31; H, 8.45.
Reaction employing Grubbs Generation I in conjunction with $[^2\text{H}_2]$-decene, example of analysis by GC and GC-MS (as shown in Scheme 4 in communication)

Sample 1 (without bromine addition): Analysed by GC and GC-MS:

(i) GC

(ii) GC/MS
(a) Enyne, 1a (m/z 210)

(b) [\textsuperscript{2}H\textsubscript{7}] reference products, [\textsuperscript{2}H\textsubscript{7}] 2a (m/z 217)

(c) Sample 1: reaction mixture: 2a (m/z 210), [\textsuperscript{2}H\textsubscript{2}] 2a (m/z 212), [\textsuperscript{2}H\textsubscript{7}] 2a (m/z 217) and [\textsuperscript{2}H\textsubscript{9}] 2a (m/z 219)
Sample 2: Bromine was added drop-wise to the second sample until its deep red colour persisted upon shaking. 1-Pentene was then added to quench any excess bromine to afford a once again colourless solution. This second sample was then also analysed by GC/MS:

(a) in-situ bromination of reference decene (deca-1,3-dienyl cation m/z 137)

(b) in-situ bromination of reference 1-[\textsuperscript{2}H_2]-decene, (1-[\textsuperscript{2}H_2]-deca-1,3-dienyl cation m/z 139):
(c) Sample 2: in-situ bromination of mixture of 1-decene and 1-$^{2}$H$_2$-decene from reaction
Kinetics of alkene exchange between ruthenium alkylidenes 3b, 3c and 3d, by $^{31}$P NMR analysis of equilibration:

![Diagram of ruthenium alkylidene exchange](image)

Typical procedure: a solution of ruthenium alkylidene A (0.024 mmol in DCM (0.4 cm$^3$)) was added via gas-tight syringe to a solution of alkene (0.024 mmol) in a mixture of DCM (0.3 cm$^3$) and d2-DCM (0.1 cm$^3$), in a 5 mm diameter NMR tube under nitrogen. The tube was sealed with a Young's valve. The resulting 0.8 cm$^3$ sample had [A]$_0$ = 30 mM and [alkene]$_0$ = 30 mM. Equilibration was monitored by $^{31}$P NMR analysis of the signals for the PCy$_3$ in alkylidenes A and B. An example NMR spectrum is shown below where RuCl$_2$(=CHCH$_2$C(CO$_2$Me)$_2$)(PCy$_3$)$_2$ (3d = A) was employed in conjunction with 1-hexene to give Ru(=CH$_2$Bu)(PCy$_3$)$_2$ (3c = B) and allyl dimethyl malonate.

![NMR spectrum](image)

Data were collected until > 80 % equilibrium had been obtained and then analysed by automated iterative fitting to a genuine bimolecular equilibrium: (A + alkene-b $<$--$>$ B + alkene-a), thus extracting $k_{ex(\text{forward})}$, $k_{ex(\text{backward})}$ and $K_{ex}$ for the pseudo bimolecular equilibrium which will also include a Cy$_3$P dissociation pre-equilibrium. The resulting datapoints and fits are shown below.
3d → hexene equilibrating to 3c → allyl dimethyl malonate

\[ k_{ex} (\text{forward}) = 0.126 \]
\[ k_{ex} (\text{backward}) = 0.0173 \quad \text{error} = 0.06 \]

3d → allyl chloride equilibrating to 3b → allyl dimethyl malonate

\[ k_{ex} (\text{forward}) = 0.0791 \]
\[ k_{ex} (\text{backward}) = 0.00113 \quad \text{error} = 0.07 \]

3c → allyl chloride equilibrating to 3b → hexene

\[ k_{ex} (\text{forward}) = 0.135 \]
\[ k_{ex} (\text{backward}) = 0.0223 \quad \text{error} = 0.03 \]
Kinetics of RCM of enyne 1a using alkene co-catalysts

All reactions were conducted according to the following general procedure: a solution of 1a (0.24 mmol, 0.06M overall), internal standard (dodecane) and additive (0.006 mmol, 0.0015M overall, 2.5 mol% to 1.2 mmol, 0.3M overall, 500 mol%) in dry DCM (2 cm³) was stirred at room temperature under nitrogen. Additive solutions were generally taken from pre-prepared stock solutions (e.g. for a 5 mol% loading (0.003M), a 100 µL aliquot was taken from a 10 cm³, 0.12M solution). A solution of catalyst (0.012 mmol, 0.003 M, 5 mol%) in dry DCM (2 cm³) was then added via gas-tight syringe. Reactions were then sampled (≈ 20 µL aliquots via 50 µL syringe) and samples quenched by passing the solution through a pad of silica-gel impregnated with a large excess of triphenylphosphine into a vial ready for analysis by GC analysis using dodecane as an internal integration standard. In some cases, e.g. allyl alcohol, allyl cyanide, the additive had a distinct inhibitory effect and the kinetics were not analysed. However, in general 1a was found to approximately decay according to a simple pseudo first-order rate law and thus kOBS values were extracted by linear regression of plots of ln(1/x1a) - where x1a is the mol-fraction of 1a remaining and {x1a}(t=0) = 1 – versus time (t). The value of t0 is not the time at which the catalyst was added and thus there is a positive y-axis intercept in the plot. Due to progressive catalyst deactivation and cross-metathesis, rates deviated significantly from apparent non-first order behaviour above a certain threshold of conversion, depending on the additive being used. These thresholds ranged from ca. 25 % (no additive) to > 85% and data above the thresholds were excluded from the linear regression analysis. Representative decays and associated linear regressions of ln(1/x1a) versus t for 1a with 20 , 100 and 200 mol% hexene are shown below.

**IMPORTANT**: the reaction kinetics (kOBS) were found to vary by up to 2-fold between different batches of 3a. Thus single batches of 3a were used for each series of comparisons (e.g. for comparing alkene length, or for the effect of [alkene]) together with a control reaction (no additive). In all of the tabulated data below, rate constants (kOBS) should not be transposed between tables, but only within tables, to ensure that data from the same batch of catalyst is being compared. Where different batches of catalyst are employed within the same table, this is indicated. There was no obvious difference between the batches in terms of physical appearance, solution phase colour or 31P{1H} NMR spectrum (clean singlet in all cases).
Effect of simple alk-1-enes on RCM of 1a - maximum rate acceleration ($k_{SAT} / k_0$) and RCM-CM

Reactions with $n$-alk-1-enes ($C_xH_{2x}$) where $x = 2, 5, 6, 8, 10, 12, 14, 18$ were run with 500 mol% alkene, to ensure saturation, *vide infra*, and the $k_{OBS} (= k_{SAT})$ value compared with $k_{OBS} (= k_0)$ obtained in control reactions with no additive.

<table>
<thead>
<tr>
<th>$C_xH_{2x}$ x</th>
<th>$k_{OBS} (= k_{SAT})$ ($\times 10^4$ / sec)</th>
<th>$k_{SAT}/k_0$</th>
<th>$[7a]/([2a]+[7a])_{60}$ (%)</th>
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<tr>
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The rate ratios ($k_{SAT} / k_0$) which correspond to the maximum acceleration under these conditions were analysed as a function of $x$ (graph A below). In all cases (except the control reaction) the conversion of 1a was > 85% after 60 minutes and the proportion of RCM-CM product ($[7a]/([2a]+[7a])_{60}$ (%) at this point was analysed as a function of $x$; graph B (the data for dodecane appears anomalous, but was consistently low throughout the run, and is omitted from the plot).
Effect of simple \(n\)-alk-1-enes on RCM of 1a - order in alkene \(C_2H_{2x}\) where \(x = 6, 10, 14\)

Reactions with \(n\)-alk-1-enes \((C_2H_{2x})\) where \(x = 6, 10\) and 14 were run with 0 to 500 mol\% alkene and the \(k_{\text{OBS}}\) value analysed as a function of \([C_2H_{2x}]_0\).

\textit{n-hex-1-ene}

\begin{center}
\begin{tabular}{ll}
\text{\(C_6H_{12x}\)} & \text{\(k_{\text{OBS}}\)} \\
\text{mol\%} & \text{\((\times 10^4 \text{ / sec})\)} \\
0 & 1.1 \\
10 & 1.2 \\
20 & 1.8 \\
50 & 2.4 \\
100 & 3.6 \\
200 & 9.2 \\
300 & 10.0 \\
500 & 10.1 \\
\end{tabular}
\end{center}

\textit{n-dec-1-ene}

\begin{center}
\begin{tabular}{ll}
\text{\(C_{10}H_{20x}\)} & \text{\(k_{\text{OBS}}\)} \\
\text{mol\%} & \text{\((\times 10^4 \text{ / sec})\)} \\
0 & 2.3 \\
10 & 2.5 \\
20 & 2.8 \\
50 & 3.4 \\
100 & 5.4 \\
200 & 7.4 \\
300 & 7.5 \\
500 & 7.4 \\
\end{tabular}
\end{center}

\textit{n-tetradec-1-ene}

\begin{center}
\begin{tabular}{ll}
\text{\(C_{14}H_{28x}\)} & \text{\(k_{\text{OBS}}\)} \\
\text{mol\%} & \text{\((\times 10^4 \text{ / sec})\)} \\
0 & 1.7 \\
10 & 2.0 \\
50 & 4.8 \\
100 & 7.1 \\
250 & 7.6 \\
500 & 6.6 \\
\end{tabular}
\end{center}
Effect of allyl bromide on RCM of 1a

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<th>mol%</th>
<th>(k_{\text{OBS}}) (\times 10^4 / \text{sec})</th>
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References